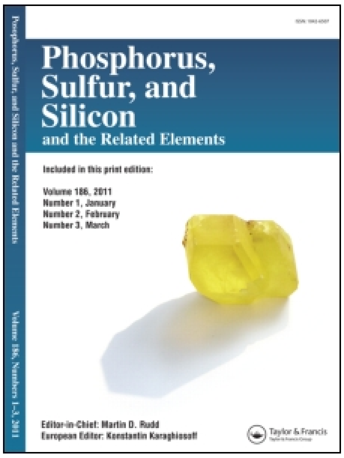

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First Example of Te-C Bond Cleaved Product in the Reaction of $C_8H_8TeI_2$ with Ammonium Pipertidine Dithiocarbamate

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First Example of Te-C Bond Cleaved Product in the Reaction of $C_8H_8TeI_2$ with Ammonium Pipertidine Dithiocarbamate

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A series of 1,3-dihydro-2λ^4-benzotellurole-2,2-diyl di-thiocarbamates $C_8H_8TeR_2$ and C_8H_8TeIR (R=$S_2CNC_5H_{10}$, $S_2CNHC_6H_5$, $S_2CNC_4H_8O$) have been synthesised by the reactions of C8H8TeI_2 with the corresponding ammonium salts of piperidine-, aniline- and morpholine-dithiocarbamates in 1:1 and 1:2 molar ratio, respectively. They have been characterized by FT-IR and (^1H, ^{13}C) NMR spectroscopy. The reaction of $C_8H_8TeI_2$ with ($NH_4S_2CNC_5H_{10}$) in 1:2 molar ratio gives $C_8H_8Te(S_2CNC_5H_{10})_2$ [IR, (^1H, ^{13}C)NMR evidence] and X-ray quality crystals of $Te(S_2CNC_5H_{10})_2$ in very low yield, demonstrating the formation of the first Te—C bond-cleaved product.The monomers of $Te(S_2CNC_5H_{10})_2$ are connected through intermolecular Te···S secondary bonds and it exists as a dimer in the solid state. These dimers are interconnected through intermolecular S···S secondary bonds to yield 3D-supramolecular network.

1,1,2,3,4,5,6-Heptahydro Tellurane Derivatives: Synthesis, Spectroscopic Characterization, and Structure of 1,1,2,3,4,5,6-Heptahydro-1,1-Dibromotellurane

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The metathetical reactions of 1,1,2,3,4,5,6- heptahydro-1,1-diiodotellurane ($C_5H_{10}TeI_2$) with AgX (X=Cl, Br, NCO, NCS) yielded 1,1,2,3,4,5,6-1,1-di-(halo) or (pseudohalo) telluranes. They were characterized by FT-IR, ^1H, and ^{13}C NMR spectroscopy. The structure of 1,1,2,3,4,5,6-heptahydro-1,1-dibromo tellurane ($C_5H_{10}TeBr_2$) was established by single crystal X-ray diffraction studies. It possessed distorted trigonal bipyramidal geometry (ψTBP). The molecules of $C_5H_{10}TeBr_2$ are linked together through Te$\cdots$Br secondary bonds resulting in trimeric aggregates which are analogous to the trimeric aggregates present in 1,1,2,3,4,5,6-heptahydro-1,1-diiodotellurane.

Selenium–An Unknown Vital Agent

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Selenium plays a very important role in physiology of human body. Selenium is not only useful for normal health of human body, but it also helpful in curing many diseases.

As an essential trace mineral in the human body, selenium is an important part of antioxidant enzymes that protect cells against the effect of free radicals that are produced during normal oxygen metabolism. With the help of selenium, the body has developed defenses such as antioxidants to contol levels of free radicals. These free radicals can damage cells and contribute to the development of some chronic diseases. Selenium also protects the body against contaminants such as mercury, cadmium, and silver; it helps speedy the elimination of cancer cells and slows tumor growth. Selenium reduces one's risk of cancer, such as cancer of the breast, colon, liver, skin, and lung. Selenium may be important in HIV disease because of its role in the immune system and as an antioxidant. Selenium is also needed for proper pancreatic function and to maintain the natural elasticity of tissue in the body. Selenium prevents heart attacks and strokes by lowering one's bad cholesterol. Selenium also keeps one's arteries clear, and free from dangerous fatty deposits. This makes it an important additional therapy after a heart attack.

For good health, daily selenium dietary intake is recommended; Children are considered to be 30 to 150 mcg or 1.5 mcg/. (0.7 mcg./ kilogram) of body weight; the usual therapeutic dosage for adults is considered to be 50 to 200 mcg/day. The percentage amount of selenium in a healthy human is 0.00002%. For best results, Selenium should be taken with vitamin E. Selenium is usually not toxic, but can be it than 400 mcg/day are taken. The toxic form of selenium is called selenois. Selenois may result is numbness or tingling in the finger or toes, white spots on fingernails and toenails, or hair loss. In lower doses than the requirement, Selenium may cause dizziness or irritability.

With the help of advanced research activities on selenium and its effect on human health and its potential use in curing complicated disease, it is likely that selenium may form a vital part in the pharmaceuticals industry in the coming years.

Bis{2-(Dimethylamino)propyl}dichalcogenides and 2-(Dimethylamino)propylchlacogenolate (Se, Te) Complexes of Pd(II) and Pt(II)

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Bis{2-(dimethylamino)propyl}dichalcogenides, $(Me_2NCH_2CHMeE)_2$ (1) $[N^{\cap}E^{*})_2]$ and $(Me_2NCHMeCH_2E)_2$ (2) $[N^{\cap}E^{**})_2]$ (E=Se, Te) have been synthesized by the reaction of M'_2E_2 (M'=Na or K) with $Me_2NCH_2CHMeCl$. In the mixture of $[(N^{\cap}E)_2]$ of 1 and 2 (E=Se, Te), ratio of **1** and **2** is chalcogen dependent. The reaction of $[(N^{\cap}E)_2]$ with Na_2PdCl_4 or K_2PtCl_4 in methanol yields sparingly soluble deep-colored complexes of the general formula $[MCl(E^{\cap}N)]_n$ (3) (M=Pd or Pt). Treatment of Na_2PdCl_4 or K_2PtCl_4 with two equivalents of $NaE^{\cap}N$, prepared by $NaBH_4$ reduction of chalcogenide in methanl, affords bis complexes $[M(E^{\cap}N)_2]_n$ (4). Reactions of $NaE^{\cap}N$ with $M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ give complexes of type $[MCl(E^{\cap}N)(PR_3)]$ (5) (PR_3=PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, $PMePh_2$, PPh_3). These complexes have been characterized by elemental analysis IR, UV-Vis and NMR (^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{125}Te, and ^{195}Pt) spectroscopy. The complexes of the series $[MCl(E^{\cap}N)(PR_3)]$ are deep-colored with absorptions varying between 400–500 nm, the absorption being blue shifts (~80 nm) in platinum complexes as compared to corresponding palladium derivatives. The phosphine complexes (5) have an atypical pattern of mutually *trans* neutral (P and N) and anionic (Cl and E) ligands in an approximately square planar environment as reveald by single crystal X-ray crystallography. Thermal behavior of few complexes has been investigated.

Chalcogenides of Phosphorus Ligands: Synthesis, Reactivity and Transition Metal Chemistry

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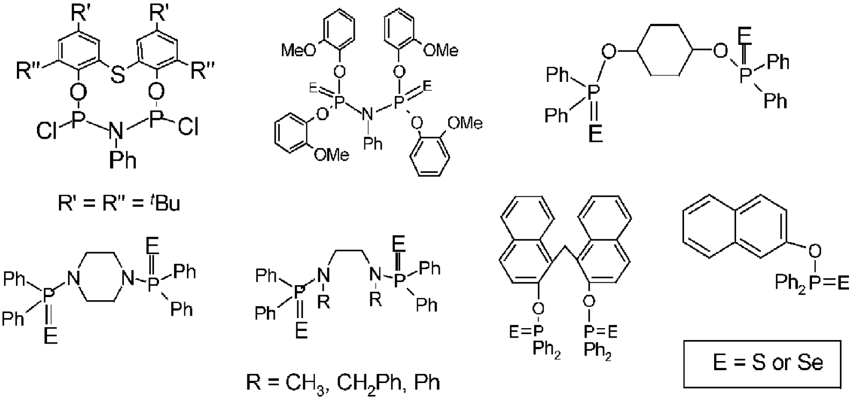
Potentially tridentate inorganic heterocycle containing sulfur and trivalent phosphorus centers $PhNP(Cl)\{(OC_6H_2(t\mathrm{Bu})_2)(\mu\text{-}S)((t\mathrm{Bu})_2C_6H_2O\}P(Cl)$ was prepared by reacting $Cl_2PN(Ph)PCl_2$ with $HOC_6H_2(t\mathrm{Bu})_2)(\mu\text{-}S)((t\mathrm{Bu})_2C_6H_2OH$ in good yields. Several bisphosphines with a variety of spacers and functionalities such as $PhN(P(OC_6H_4OMe\text{-}o)_2)_2$, $Ph_2O(C_6H_{10})OPPh_2$, $Ph_2PN(C_4H_8)NPPh_2$, $(Ph_2PN(R)CH_2)_2$ ($R{=}CH_3$, CH_2Ph and Ph), $Ph_2P\{(\text{-}OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O\text{-}\}PPh_2$, and $C_{10}H_7OPPh_2$ were prepared as derivatives of $PhN(PCl_2)_2$ or Ph_2PCl. The phosphorus centers of these compounds react smoothly with elemental sulfur or selenium to give the corresponding sulfides or selenides in quantitative yield. Reactions of $PhNP(Cl)\{(OC_6H_2(t\mathrm{Bu})_2)(\mu\text{-}S)((t\mathrm{Bu})_2C_6H_2O\}P(Cl)$ with palladium(II), platinum(II), rhodium(I), ruthenium(II), and molybdenum(0) derivatives afforded the corresponding metal complexes with ligand, exhibiting a variety of coordination modes. Reaction of $PhN\{P(S)(OC_6H_4OMe\text{-}o)_2\}_2$ with $[Cu(NCMe)_4]BF_4$ afforded a



SCHEME 1

bischelated transition metal complex, $[Cu\{PhN((S)P(OC_6H_4OMe\text{-}o)_2)_2\}_2]BF_4$. The details of synthesis, reactivity, and spectroscopic and structural aspects are presented, (Scheme 1).

Synthesis and Characterization of a Bulky Tri(organosilyl)methyl Ligand Containing a SePh Donor Group

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There is discernible growth in interest in the synthesis of bulky tri(organosilyl)methyl ligands of the type $C(SiMe_3)_n(SiMe_2X)_{3-n}$ where X is a donor group because of their rich organometallic chemistry.[1,2] The introduction of the functionalized donor group at the silicon is due to the fact that they have lone pairs and are capable of coordinating intra- or inter-molecularly to the metal. Keeping this in view, the present paper reports the synthesis and crystal structure of $CH(SiMe_3)_2(SiMe_2Br)$ and its conversion into a new bulky ligand $CH(SiMe_3)_2(SiMe_2SePh)$.

The $CH(SiMe_3)_2(SiMe_2Br)$ has been synthesized by bromination of the hydride $CH(SiMe_3)_2(SiMe_2H)$ obtained from the reaction between $CH(SiMe_3)_2Br$ and Me_2SiHCl and has been characterized by ^1H, ^{13}C, ^{29}Si NMR, mass spectroscopy, and crystal structure determination. The Si—C—Si bond angles are widened by steric interaction between $SiMe_3$ groups from the tetrahedral value to an average of 114.98(13)°. The mean Si—Cl bond length to the central carbon and Si—Br bond lengths are 1.886(2) and 2.243(2) Å, respectively. Treatment of the bormide with NaSePh, obtained by sodium triethylborohydride reduction of PhSeSePh, gives the compound $CH(SiMe_3)_2(SiMe_2SePh)$ as yellow oil, which has been characterized by multinuclear NMR and mass spectrometry.

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On the Relative Stabilities of Molecular Complexes Versus Trigonal Bipyramidal Adducts, Together with the Components in Selenide Dibromides in Solutions

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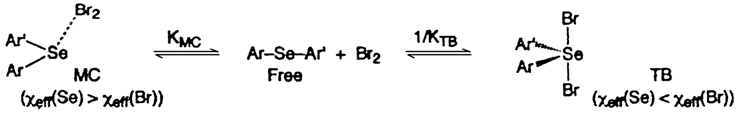
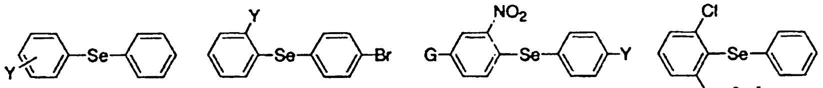
Diaryl selenides (ArSeAr′) react with Br_2 to give trigonal bipyramidal adducts ($ArSeBr_2Ar'$ (TB)), since the electronegativity of Se (χ(Se) = 2.48) is larger than that of bromine (χ(Br) = 2.74). The adducts will be molecular complexes (MC) if the effective electronegativitiy of selenium (χ_{eff}(Se)) and/or the steric congestion around the atom in ArSeAr′ is chemically increased. Therefore, $ArSeBr_2Ar'$ (MC) should be essentially in equilibrium with $ArSeBr_2Ar'$ (TB), together with the components, in solutions Scheme 1.[1–4]



(1)

SCHEME 1



1a, b, d, h, i for 4-Y; **2e–g** for 2-Y

3e–g

4a, c, f for G = H; **5a, c, f** for G = NO_2

6a,f

	a	b	c	d	e	f	g	h	i
Y =	H	OMe	t-Bu	Me	Cl	Br	I	COOEt	NO_2

SCHEME 2

The equilibrium constants (K_{MC} and K_{TB}) for $ArSeBr_2Ar'$ (MC) and $ArSeBr_2Ar'$ (TB), together with the molar fractions, are determined based on the NMR chemical shifts for **1–6** (Scheme 2). QC calculations are also employed to explain the relative stability of the adducts. Research highlights will be presented.

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First Isolation of a Novel-Air Stable Mercury Tellurolate and the Preparation of CdS and CdSe Nanoparticles from the Respective Cadmium Chalcogenolates

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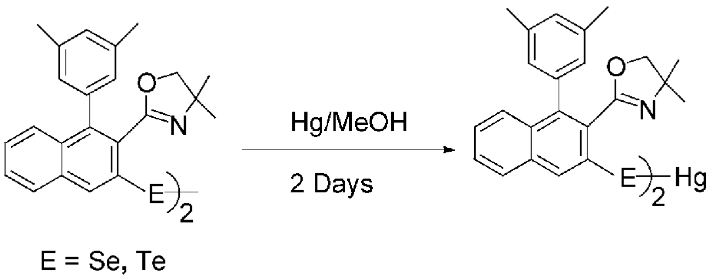
In general, monomeric group 12 metal chalcogenolates are difficult to obtain due to formation of polymeric or oligomeric complexes through bridging of chalcogenolate ligands.[1] Several possible approaches have been employed to isolate the stable monomeric mercury chalcogenolates.[2–4] However, efforts to extend these approaches to tellurolate chemistry have resulted in the formation of polymeric complexes[5] or a reductive elimination of the complex to give a dichalcogenide and elemental metal.[2–4] We report the preparation and characterization of mercury chalcogenolates using [2-[1-(3,5-dimethylphenyl)-2-naphthyl]-4,5-dihydro-4,4-dimethyloxazole] having both sterically



SCHEME 1

more demanding and intramolecular-coordinating features. Also the preparation and characterization of CdS and CdSe nanoparticles from the corresponding cadmium chalcogenolates[6,7] has been reported since this class of compounds has been demonstrated as single-source precursors for the preparation of nano/bulk size 12–16 semicondutors.[8]

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Ethyl Selenolato Bridged Dinuclear Pd(II) and Pt(II) Compounds

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Ethyl selenolato bridged dinuclear palladium(II) and platinum(II) compounds of the type $[M_2Cl_2(\mu\text{-Cl})\ (\mu\text{-SeEt})(PR_3)_2]$ (where M=Pd or Pt; PR_3=PBu_3, PEt_3, PMe_2Ph or $PMePh_2$) were prepared by the reaction of $[M_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ with one equivalent of NaSeEt in CH_2Cl_2 methanol mixture. All these compounds have been characterized by CHN analysis, and ^1H and ^{31}P NMR spectroscopic techniques. The ^{31}P NMR spectra of all these compounds showed that they exist in a *cis* geometry with the bridging SeEt group *trans* to the terminal chloride. The structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\text{-}\mu\text{-}SeEt)(PMe_2Ph)_2]$ has been determined by the single crystal X-ray diffraction method and is in agreement with the spectroscopic observations. The crystal is Orthorhombic [Pnma(#62)] with the cell parameters, a = 11.534(2) Å, b = 19.893(2) Å and c = 10. 856 (1) Å. The observed bond (average) distances, 2.390(2) Å, 2.336(5) Å, 2.425 (5) Å, and 2.211(5) Å are for the Pt-Se, Pt-Cl (terminal), Pt-Cl (bridging), and Pt–P, respectively.

Synthesis of N,N-Dimethylalkylselenolate Complexes of Group II: Molecular Precursors for Metal Selenides

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N,*N*-Dimethylalkylselenolate complexes of Zn, Cd, and Hg of the general formula $[M\{Se(CH_2)_nNMe_2\}_2]$ (**1**), (M=Zn, Cd, Hg; n = 2 or 3) have been synthesized. All the complexes have been characterized by elemental analysis and NMR (^1H, ^{13}C, ^{77}Se) spectroscopy. Several reactions of **1** with various nitrogen and phosphorous donor ligands have been investigated. Structures of some of these have been established by single crystal X-ray analysis. The TG response of $[Zn(SeCH_2CH_2NMe_2)_2]$ showed two overlapping decomposition steps, leading to ZnSe (from weight loss and XRD pattern) at 260°C. Thermolysis of substantial amount of precursors $[M(SeCH_2CH_2NMe_2)_2]$, (M=Zn, Cd) and $[M(SeCH_2CH_2CH_2NMe_2)_2]$, and (M=Zn, Cd, Hg) at ~350°C yield corresponding MSe (from weight loss and an XRD pattern). The XRD pattern of the residue from thermolysis of cadium complexes shows that CdSe has the cubic phase.